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Final Technical Report

'Molecularly Designed Auxetic Polymers: A Remarkable New Class of Materials'
AFOSR Grant F49620-94-1-0454

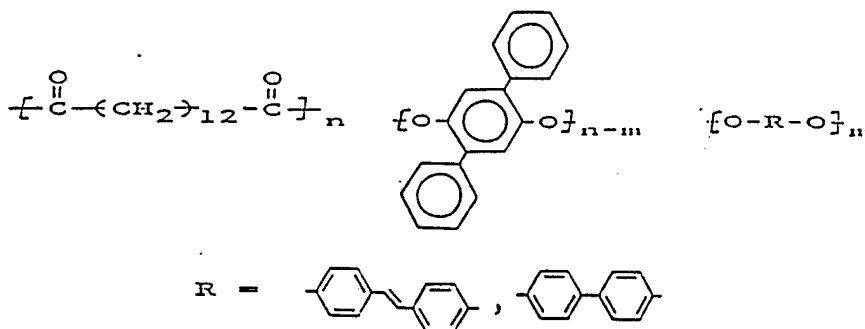
Anselm C. Griffin
Departments of Chemistry & Biochemistry and Polymer Science

Sept. 29, 1994 – Sept. 30, 1997

In this final technical report information from the interim technical reports from years 1 and 2 is combined with a description of the activities in year 3. Over the three-year duration of this project the evolution of the focus always to better candidate polymers can be seen.

During this first year of the grant period, the key personnel were brought on board- Dr. Bertrand Guichard from Paris and Puwei Liu a new PhD student at USM. The target monomers were selected and synthetic work was begun. Two general synthetic plans were followed: one to prepare an 'inverted honeycomb/reentrant cell' macrocycle and the other to prepare monomers for a main chain liquid crystalline polymer. The first of these, the macrocycle, was sought to examine the idea that in-plane stretching deformation of such a structure could lead to a negative Poisson ratio material. In turn a network of such reentrant cells could produce- by a flexing or hinging motion- a polymeric negative Poisson ratio material. Synthetic work along these lines, although interesting in its own right, did not produce the desired macrocycle. Instead, there was premature macrocycle formation early in the synthetic route which- although producing intriguing new macrocycles- did not advance this area of the project. After numerous attempts at this target, it was decided to concentrate exclusively on the second approach- the main chain liquid crystalline polymer approach.

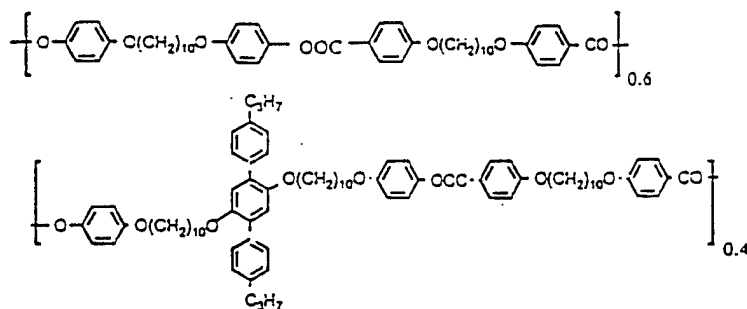
It was decided to prepare a polyester liquid crystal which would be composed of flexible spacers and of rods, most of the rods were to be attached to the spacers in the 'ordinary' way- terminally- with some attached side-on or laterally. The mechanistic origins of a negative Poisson ratio (auxetic) response in this type of polymer has been described in the original proposal. The specific chemical structures below were chosen as our first targets and they were prepared, purified and characterized.



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These polymers were indeed liquid crystalline and they incorporated the anticipated amount of transverse rods in their structures. Even though they were random copolymers they were, unfortunately, smectic- not nematic. Several polymeric compositions were prepared and examined by GPC, scanning calorimetry, optical microscopy and x-ray diffraction. All were smectic. It was our contention that a nematic polymer would be best for our purposes since less resistance would be involved in the displacement of adjacent chains during the rod reorientation process necessary for our polymer to exhibit the auxetic effect. It was concluded that we should turn our attention to a nematic parent polymer for future structural modification.

Year two of this grant saw the project focus on main chain liquid crystalline polymers. It was concluded from the first year's work that we wanted a nematic polymer in order to have the optimal combination of imposed orientational order in the quiescent state, yet have a reasonably facile reorientation of the laterally attached rods under an applied stretching force. After considerable searching of the literature for an appropriate nematic main chain polymer suitable for structural modification to allow incorporation of a laterally-attached rod component, we chose a simple family of nematic polyesters which we had made several years back. We also undertook the complex, multi-step preparation of monomers which would contain the laterally-attached rod, yet would produce only minimal disruption of the intrinsic nematic ordering. The chemical structure of a specific example of these new target polymers is shown below.



It was gratifying to find that this type of polymer had the anticipated incorporation of the laterally-attached rods and that they were indeed nematic. We sent samples of these polymers to Prof. Ken Evans at the University of Exeter who reported to us that his preliminary investigation revealed a possible negative value of the Poisson ration for these polymers. This was exciting for us and we began to prepare more polymer and more thick film samples for him. After much effort and numerous samples, it was tentatively concluded that our original thick films likely had experienced a

compressional force during their preparation which led to a flow-induced orientation which in turn was responsible for this encouraging preliminary finding. We concentrated on the synthesis of higher molecular weight polymers and on the preparation of thick film samples having some degree of flow-induced orientation. At the end of this second year we were convinced we had settled on the right family of nematic main chain liquid crystalline polymers and were actively working on the details of sample preparation for auxetic measurement.

The third year of the project was primarily focused on materials characterization of the polymers with some new synthetic target monomers being examined as well. The most exciting result of this period was the finding – using x-ray scattering techniques – that our concept of site-connectivity driven rod reorientation was proved at the molecular scale. X-ray studies of powder (unoriented) samples and fiber (oriented) samples clearly revealed that, in contrast to the powders, the stretched fibers showed an increase in the average interchain distance. This means that the transverse rod reorientation is forcing neighboring chains further apart as predicted from our model. This molecular effect should be translated to auxetic response under appropriate conditions. In addition we continued to examine origins of the highly unusual finding of anisotropic Poisson's ratios in a rectangular plaque of our polymer. Experiments performed by Prof. Ken Evans at Exeter showed that in two directions, both perpendicular to the stretch direction, the Poisson's ratio was very different; one being 0.9 and the other, 0.07. The extreme anisotropy of the Poisson's ratios is unprecedented and is currently being further examined. On the synthetic front much effort was devoted to synthesis of 2,6 rather than 2,5 substitution patterns for connecting the polymer chain to the central aromatic ring of our transverse rods. Molecular models suggest that the 2,6 pattern can lead to complete perpendicularity of the transverse rod upon application of a stretching force. This is some 30 degrees better than that possible for the 2,5-patterned rods. In spite of our best efforts we were unable to devise and execute a reasonable synthesis of a suitable 2,6-patterned transverse rod monomer. It is worthy of note that we also had activities directed toward the processing of our polymeric materials into films suitable for study by our collaborators in Exeter. The conditions for producing a thick film with uniform thickness and consistency as well as with predetermined shear orientation was thoroughly researched.

In summary the project went forward over the grant period on the design and synthesis front with corresponding attention to characterization as polymeric materials were produced. Our collaboration with UK scientists were fruitful and led to new materials and a refining of concepts on our end. We feel we have demonstrated the soundness of our site-connectivity driven rod reorientation concept as a viable approach to establishing predictive structure/property relations for auxetic polymeric materials.

Program Statistics (1994-1997)

- (1) number of PI's involved in the research project: 1
- (2) number of postdocs supported over the project period under AFOSR: 2
- (3) number of graduate students supported over the project period by AFOSR: 1

- (4) other researchers supported over the project period by AFOSR: 0
(5) number of publications by PI over the project period in refereed journals: 12
(6) number of publications (refereed) that acknowledge AFOSR support – this grant: 2
(7) awards and honors received by the PI (life-time): 7

Transitions

a. Griffin, Univ. of Southern Miss. b. liquid crystalline polymers having transversely-attached rods c. K.E. Evans, Univ. of Exeter, 44-1392-263648 d. mechanical examination of our polymers

Listing of Specifics:

- (1) Anselm C. Griffin
- (2) Bertrand Guichard, Chaobin He
- (3) Puwei Liu
- (4) none

(6) "Toward Negative Poisson Ratio Polymers through Molecular Design", Chaobin He, Puwei Liu and Anselm C. Griffin, Macromolecules, 31, 3145-3147 (1998);

"Orientational Susceptibility and Elastic Constants Near the Nematic-Isotropic Phase Transition for Trimers with Terminal-Lateral-Lateral-Terminal Connections", Daeseung Kang, Milind P. Mahajan, Rolfe G. Petschek, Charles Rosenblatt, Chaobin He, Puwei Liu and A.C. Griffin, Phys. Rev. E, 58, 2041 (1998).

Unrefereed: "Liquid Crystalline Polymers as Potential Auxetic Materials", Puwei Liu, Chaobin He, Anselm C. Griffin, ACS Polymer Preprints, 38(2), 251-252 (1997)

(7) 'Excellence in Teaching Award', 1976, USM; 'Faculty Research Award', 1980, 1988, USM; 'Outstanding USM Faculty Member Award and Recognition by the Mississippi State Legislature', 1989, USM; chair, Gordon Research Conference on Liquid Crystals, 1989; named 'Polymer Science Pioneer' by Polymer News, 1993; appointed to position of Director of the Melville Laboratory for Polymer Synthesis; Univ. of Cambridge, 1993; appointed as Bennett Distinguished Professor, 1993; USM.